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Stripping of Organic Chemicals in Biological Treatment Processes

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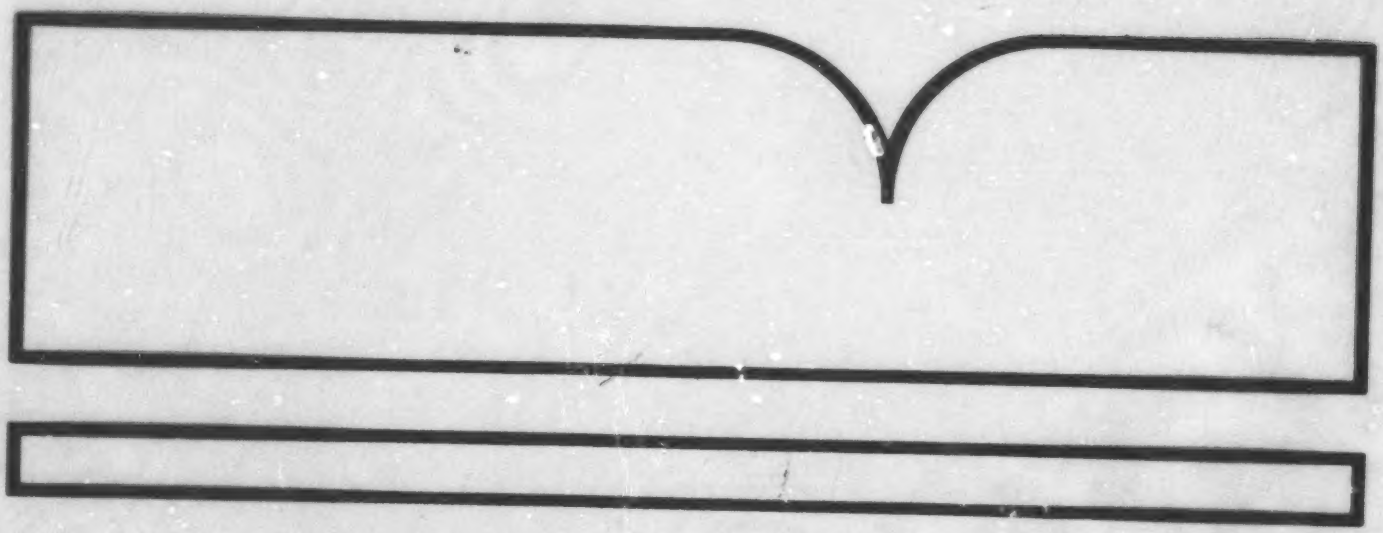

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THE STRIPPING OF ORGANIC CHEMICALS IN BIOLOGICAL TREATMENT PROCESSES

by

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Contracts 68-03-3027 and 68-03-3074

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16. ABSTRACT

An approach was developed in order to measure, then predict the fates of organic chemicals in biological processes. This approach is called stripping predictive fate method (PFM). The method offers a simpler approach for estimating stripping rates from pure water and wastewater.

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ABSTRACT

Following a literature survey on the stripping of organics from water, an approach was developed to first measure, then to predict the fates of organic chemicals in biological processes. This approach endeavors to develop experimental and mathematical stripping protocols and is called a stripping predictive fate method (PFM). An experimental apparatus was designed to yield scalable data on stripping rates and to simulate an operating treatment plant as closely as possible. Over forty experiments were performed on four different compounds (toluene, 1,4-dichlorobenzene, methyl ethyl ketone, and phenol) at temperatures of approximately 20°C. A 6-in. diameter by 6-ft high glass column equipped with a coarse bubble diffuser was used. Air at constant humidity was fed into the system at flow rates of 2, 4, and 8 L/min of air to 26 L of wastewater or from 0.077 to 0.308 liters per minute per liter of wastewater. We feel that these air flow rates approximate those in full scale activated sludge plants.

This method offers a simple approach for estimating the stripping of organic chemicals from biological treatment systems, given physical property information on the chemical stripped and design data on the treatment plant. The method incorporates the Henry's law constant and the air flow to liquid volume ratio to directly yield the first order stripping rate constant in a power relationship for pure water systems. The stripping rate equation may be coupled with bio-oxidation rates and other mechanism rates to determine the overall fate of a chemical in a treatment system. The presence of surfactants, salts, oils, and nonviable biomass was found to vary the stripping rate.

The stripping PFM was tested in continuous lab-scale activated sludge units. The measured toluene stripping rate was found to be consistent with the predicted toluene stripping rate constant. It is also successfully compared to stripping rates reported by other investigators. This suggests that the stripping PFM, after testing on other chemicals, may be useful for the prediction of compound stripping in "real world" wastewater treatment processes.

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INTRODUCTION

Wastewater treatment plants often receive volatile compounds in their influent from industrial discharges or from other sources. The removal of the refractory pollutants and chemicals from water bodies to the atmosphere by the stripping mechamism can be an important environmental pathway in wastewater treatment facilities.

Stripping is distinguished from volatilization in this paper by the mode of gas-liquid contact. Stripping is the process of gas/liquid mass transfer in systems with dispersed gas or liquid phases. Volatilization occurs at the major surface between gas and liquid phases. Stripping processes normally have a much greater interfacial area and may often be more turbulent than volatilization processes.

The work presented in this paper was performed for the Environmental Protection Agency and is taken from the project report.[1] Further details on data, methods, or findings may be found in that document.

The stripping of chemicals dissolved in water can be expressed in the first order kinetic process as

$$-r^{st} = -\frac{dC_a{}^{st}}{dt} = -K_a{}^{st}{}_a\, C_a \qquad (1)$$

Where:

r^{st} = the rate equation for stripping of substrate from the aqueous compartment into the gas-vapor compartment,

$\frac{dC_a{}^{st}}{dt}$ = instantaneous rate of change of substrate concentration in the aqueous compartment related only to stripping of substrate into the gas-vapor compartment,

$K_a{}^{st}{}_a$ = substrate stripping rate constant based on aqueous phase disappearance (hr^{-1}),

a = interfacial area (m^2), and

C_a = substrate concentration in the aqueous compartment (mg/L).

In applying the two-film mass transfer model for volatilization processes, Liss and Slater[2] and Mackay and Leinonen[3] have shown that:

$$K_a{}^{st}a = \frac{a}{V}\left(\frac{1}{k_l{}^{st}} + \frac{RT}{H_c\, k_g{}^{st}}\right)^{-1} \qquad (2)$$

Where:

$k_l{}^{st}$ = liquid film mass transfer coefficient of the substrate (m hr^{-1}),

$k_g{}^{st}$ = gas film mass transfer coefficient of the substrate (m hr^{-1}),

V = total of the fluid volume (m^3),

R = universal gas constant (62.4 torr L/g-mole °K),

T = absolute temperature (°K), and

H_c = Henry's law constant (torr L/g-mole).

Similar equations can be applied to the oxygen transfer:

$$K_a{}^{o}a = \frac{a}{V}\left(\frac{1}{k_l{}^{o}} + \frac{RT}{H_c\, k_g{}^{o}}\right)^{-1} \qquad (3)$$

Where:

$K_a{}^{o}a = K_L a$ = oxygen reaeration rate constant (hr^{-1}), and

$k_l{}^{o}$, $k_g{}^{o}$ = oxygen liquid and gas film mass transfer coefficient, respectively.

The $k_g{}^{o}$ in a wastewater system is often negligible. Environmental engineering convention demands the symbol $K_L a$ to describe oxygen transfer. This study will also use $K_L a$ for oxygen transfer.

Smith and other authors[4,5,6] have shown that the volatilization rate of chemicals can be controlled by mass transfer resistance in the liquid phase (for high volatility compounds), gas phase (for low volatility compounds) or a combination of both (transition volatility compounds), depending on the value of H_c. The volatilization rate constant for high volatility compounds, with values of H_c >3500 torr L/g-mole (0.0044 atm m^3 g-$mole^{-1}$) at 25°C is. . .

$$\frac{K_a^{st}{}_a}{K_L a} = \frac{k_1^{st}}{k_1^{o}} = \left(\frac{D_L^{a}}{D_L^{o}}\right)^m = \text{constant} \qquad (4)$$

Where:

m = between 0.5 and 1.0, and

D_L^{a}, D_L^{o} = molecular diffusion coefficient of substrate and oxygen in the liquid phase, respectively.

Similar relationships may be derived for low and transition volatility compounds. This approach has been tested and has shown that if the values of chemical diffusion coefficients are known, the values of the volatilization rate constant of these chemicals can be obtained for natural water systems.[5]

This study seeks to determine suitable experimental methods for collecting stripping rate data, then to test mathematical predictive methods based on the two-film theory, to determine if they might be applied to biological treatment processes.

EXPERIMENTAL METHODS

Over forty experiments (47) were performed to obtain the stripping rate constants and the oxygen reaeration rate constants of 4 different compounds (toluene, 1,4-dichlorobenzene, methyl ethyl ketone, and phenol) in pure water and in solutions of various substances such as surfactants (Triton® DF-12, Marasperse®, Tamol®, D-Foam® ST), oil (1-octanol), salt (NaCl), foul condensate (a pulp mill waste stream), and nonviable biomass at three levels of air flow rate (2 L/min, 4 L/min, and 8 L/min). The liquid volume in the reactor was kept at a constant level of about 25.7 L and at a temperature of 20 ± 3°C.

The basic equipment used (Fig. 1) consisted of a 6-ft high, 6-in.diameter glass column equipped with a coarse bubble diffuser to introduce the air. The coarse bubble diffuser was made from a 2½-in. 304 SS threaded pipe cap. The top of the cap was milled flat and eight 1/32-in. diameter holes were drilled evenly around a 1-3/4-in. diameter concentric circle.

Air at about 12% constant humidity was fed into the system from the building supply through a pressure reducer, a regulator, a pressure meter, a 2-ft by 2½-in. carbon filter, a pressure relief valve, an air rotameter, a YSI model 91 dew point hygrometer, an air reading thermometer, and an inlet pressure reading manometer.

Liquid sample was taken from the bottom of the reactor in a ¼-in. OD 304 SS tube located in the middle of the column about 2½ ft from the bottom.

Solution was pumped to the bottom of the column by a SATURN® Model SP-3000 Teflon pump. Nitrogen was purged to the bottom of the system at the diffuser level, through a ¼-in. OD 304 SS tube entering from the top. Outlet pressure was measured with a manometer placed at the condenser inlet line.

The oxygen concentration was measured with a YSI model 54A dissolved oxygen meter with the probe hanging upside down in the middle of the column at the same level as the top of the liquid sampling line. Other analytical methods are discussed in the project report.[1] Solution temperature was measured from a thermocouple at about 3 in. below water level.

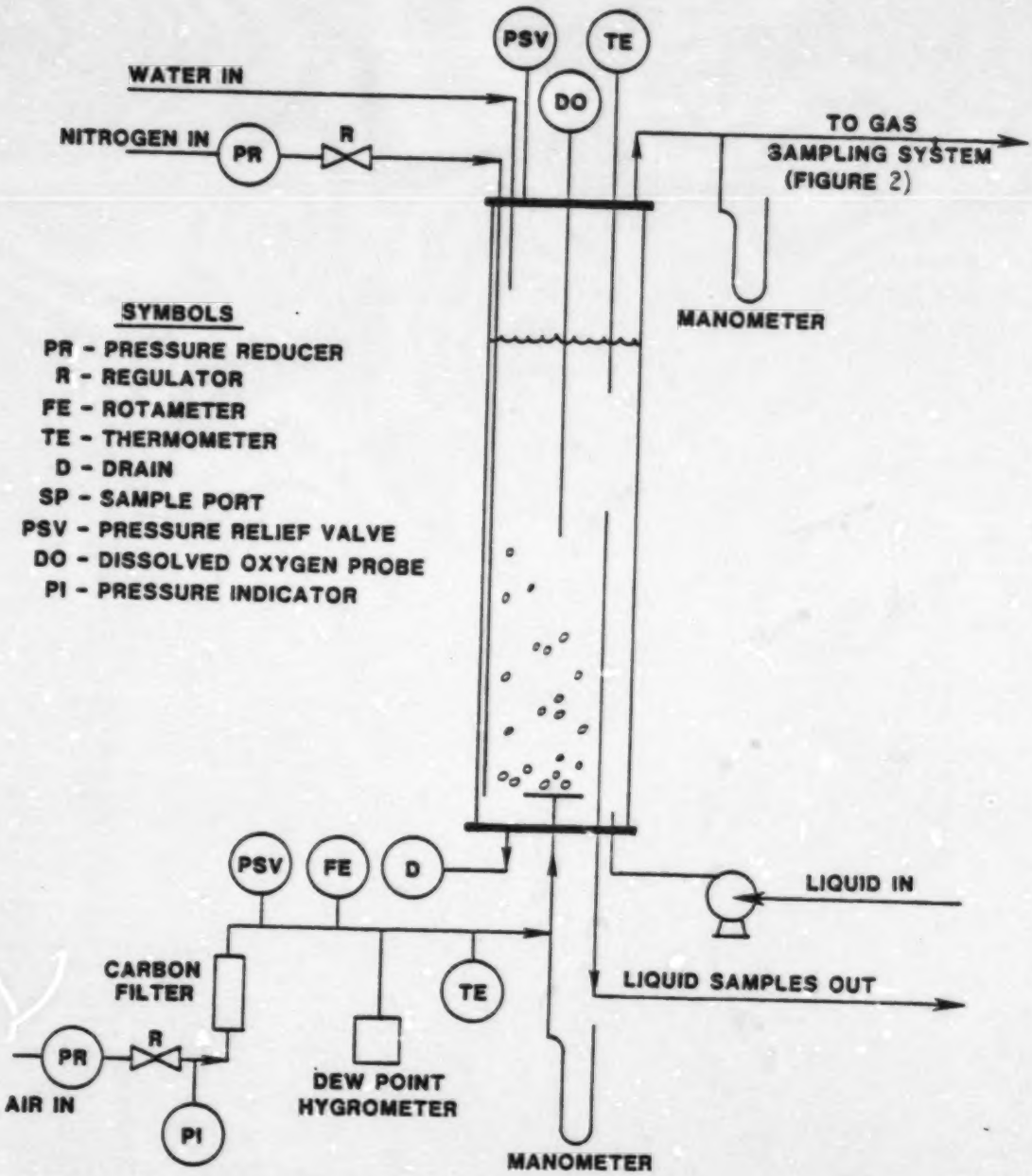

FIG. 1. APPARATUS USED IN THE STRIPPING EXPERIMENTS

A train of three 250-mL bubblers was connected at the outlet air line (Fig. 2) for 1,4-dichlorobenzene and phenol experiments. One hundred and fifty mL of isooctane or 0.1N NaOH in each bubbler was used to absorb 1,4-dichlorobenzene or phenol, respectively, for the off-gas analysis. The bubblers were not required for toluene and methyl ethyl ketone experiments; instead, an air sample port was added at the condenser outlet line. Outlet air flow was checked by an outlet rotameter placed next to the sample port.

In some of the toluene experiments the equipment described above was used; in the remaining toluene experiments, 5 Tedlar air bags were connected at the outlet line for the first 5 min of air sampling to spotcheck the syringe air analysis. Sampling of the outlet air allowed the calculation of a material balance for the more volatile compounds.

Surface tension was measured in all experiments by using a Cenco-Dunouy Model 70535 tensiometer. About 100 mL of aqueous solution was needed and three to four samples were required for each experiment.

To assure complete mixing of the starting solution, a Bench-Scale Model 7104-EHB 5/8-hp power mixer was used to dissolve the chemicals into the solution.

The Henry's law constant of the compounds studied was calculated by applying the following equations from Dilling.[7]

$$H_i = \frac{C_{air}}{C_{water}} = \frac{16.04\ PM}{TS}$$

and $$H_c = H_i\ RT$$

or $$H_c = 13.16 \times 10^{-4}\ \frac{PM}{S} \qquad (5)$$

Where:

H_i = Henry's law constant (dimensionless),

H_c = Henry's law constant (atm m^3/g-mole),

P = vapor pressure of the pure compound (mm Hg),

S = Solubility of the solute in water (mg/L),

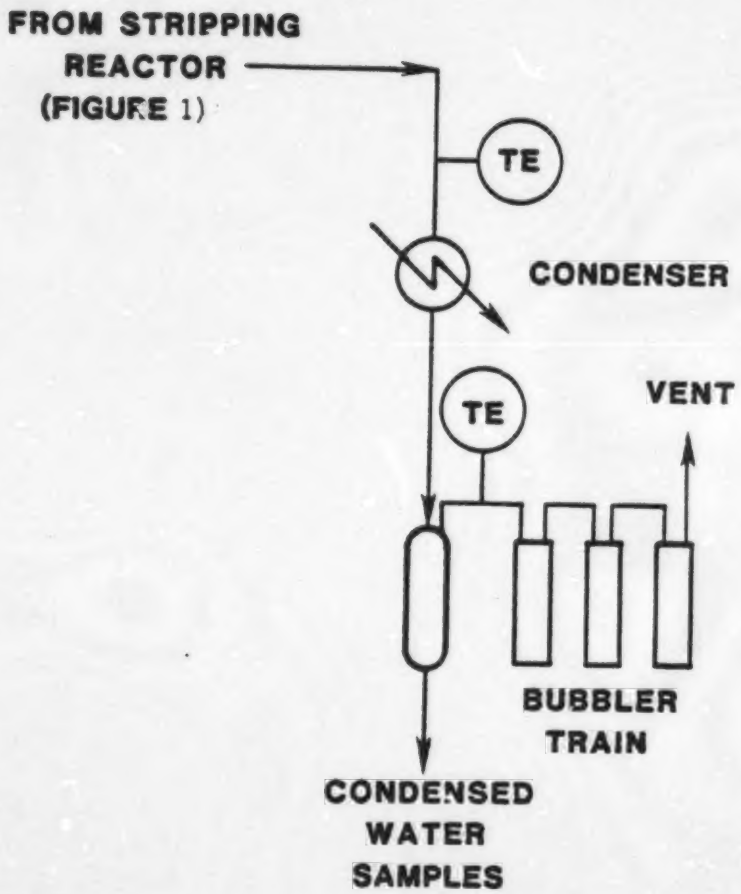

FIG. 2. GAS SAMPLING APPARATUS

M = gram-molecular weight of the solute,

T = temperature (°K), and

R = gas law constant = 8.2057 X 10^{-5} atm m^3/g-mole °K.

The value of S and P were obtained mostly from the ISHOW data base.[8] The calculated values of H_C for four compounds studied can be found in Table 1.

The general laboratory procedure for measuring stripping rate constants was to prepare a homogenous solution of chemical at a concentration below its solubility limit, then analyze the aqueous concentration of the compound at regular intervals. Measurement of the oxygen reaeration rate constant was made for each experiment by purging the solution with nitrogen and then measuring the dissolved oxygen concentration as a function of time.

For a reproducible procedure, the test compound was well mixed in water before any secondary contaminant was added. The solution was mixed again, and was observed to be completely clear, indicating that all the chemical was dissolved, before it was pumped to the reactor. The solution was then deoxygenated by purging with nitrogen. Air was allowed to diffuse to the reactor at a preset air flow rate. The 1-octanol-toluene experiment was an exception. In that experiment, 1-octanol was injected to the bottom of the column through the inlet feed valve before the toluene solution was pumped to the reactor, since it was desired to test stripping in the presence of an oil phase.

Because of 1,4-dichlorobenzene's low solubility (79 mg/L at 20°C) and the difficulty of dissolving it in water, crystalline 1,4-dichlorobenzene was suspended in pure water and mixed by a small stirrer or a magnetic stirrer in several 4 L glass containers. These reached a concentration of about 50 mg/L one or two days before the experiment. The solution was then filtered through a 20-in. diameter Whatman folded filter paper and mixed by the power mixer to obtain a homogeneous batch. The filtered solution was observed to be completely clear before it was pumped to the reactor.

Nonviable biomass was prepared by lyophilization of municipal sludge, then dry heat treatment for 5 hours. An amount of nonviable dried biomass was added to about 2.5 L of pure water and stirred with a magnetic stirrer for 30 min. It was then pumped to the reactor before pumping the chemical solution. 25.7 L of

TABLE 1. PHYSICAL PROPERTIES OF THE COMPOUNDS STUDIED

	Toluene	1,4-Dichloro-benzene	Methyl ethyl ketone	Phenol
Molecular weight	92.1	147	72.1	94.11
Specific gravity	0.866	1.458	0.805	1.071
Boiling point (°C)	110.8	173.4	79.6	182.0
Vapor pressure[a] (mm Hg at 20°C)	22.0	0.6	77.5	0.2
Solubility[a] (mg/L at 20°C)	732.0	79.0	322,600	74,500
Henry's law constant[b]				
$\frac{(atm - m^3)}{(g\text{-}mole)}$	3643×10^{-6}	1469×10^{-6}	22.8×10^{-6}	0.33×10^{-6}
$\frac{(torr\ L)}{(g\text{-}mole)}$	2769	1116	17.3	0.25

[a]From "ISHOW" data base.[8]

[b]Calculated from Dilling.[7]

chemical-biomass solution was added to yield a final concentration of about 1500 mg/L of biomass on a dry basis. The chemical-biomass solution in the reactor was purged with nitrogen for about 10 to 15 min before starting an experiment.

The dissolved oxygen concentration was read using a dissolved oxygen meter at 1- or 2-min intervals. Liquid phase analysis was performed by flushing about 25 mL of aqueous solution out of the line before an actual sample was taken for analysis, then the liquid samples were taken at a regular interval of 10 to 20 min for toluene and 1,4-dichlorobenzene and much longer for methyl ethyl ketone and phenol. The outlet air was taken for analysis at the same time as the liquid phase sample.

RESULTS AND DISCUSSIONS

The value of the stripping rate constant for each experiment was calculated from the measured values of the concentration of the chemical by using the following equation:

$$\text{Ln}\ \frac{C_{ao}}{C_{at}} = K_a{}^{st}{}_a\ (t) \qquad (6)$$

Where C_{ao} and C_{at} are the chemical concentrations at times o and t, respectively.

A plot of log C_{ao}/C_{at} versus time t is linear. The slope of the line is $K_a{}^{st}{}_a/2.3$. Therefore a stripping rate constant $K_a{}^{st}{}_a$ may be obtained. A typical plot for the results of an experiment with toluene in pure water (2 L air/min) is shown in Fig. 3. The $K_a{}^{st}{}_a$ values were obtained by using the "curve fitting" logarithmic curves of form $y = a + b \ln x$ for all experiments and are listed in Tables 2, 3, 4, and 5.

Similarly, the oxygen reaeration rate may be derived using the following equation:

$$\ln \frac{([O_2]_s - [O_2]_o)}{([O_2]_s - [O_2]_t)} = K_L a\ (t) \qquad (7)$$

Where:

$[O_2]_s$ = oxygen saturation concentration at the temperature of the solution, and

$[O_2]_o$ and $[O_2]_t$ = oxygen concentrations at times o and t, respectively.

A typical plot for a toluene experiment is shown in Fig. 4. $K_L a$ values for all experiments are shown in Tables 2, 3, 4, and 5.

Experiments ST-1, ST-2, and ST-3 were conducted at the same air flow rate, 2 L/min, but had different oxygen reaeration rate constants. The result of experiment ST-1 was considered unreliable due to the incorrect reading of the initial dissolved oxygen concentration and the difficulty of preparing toluene solution in deoxygenated water. Tap water was used in experiment ST-2 and deionized (DI) water in experiment ST-3; the results of these two experiments

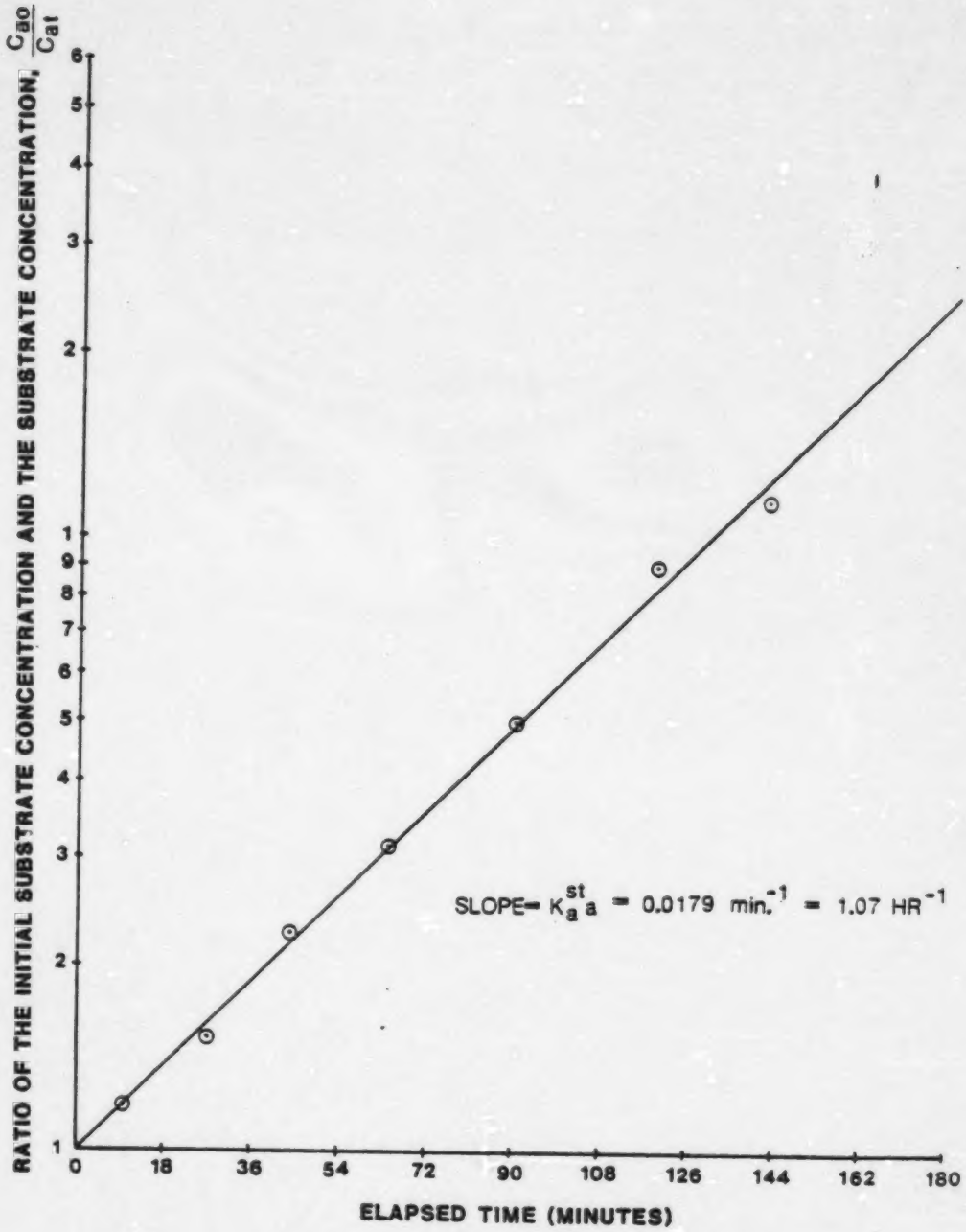

FIG. 3. DETERMINATION OF THE STRIPPING RATE CONSTANT, $K_a^{st}a$, IN EXPERIMENT ST-3, FOR TOLUENE

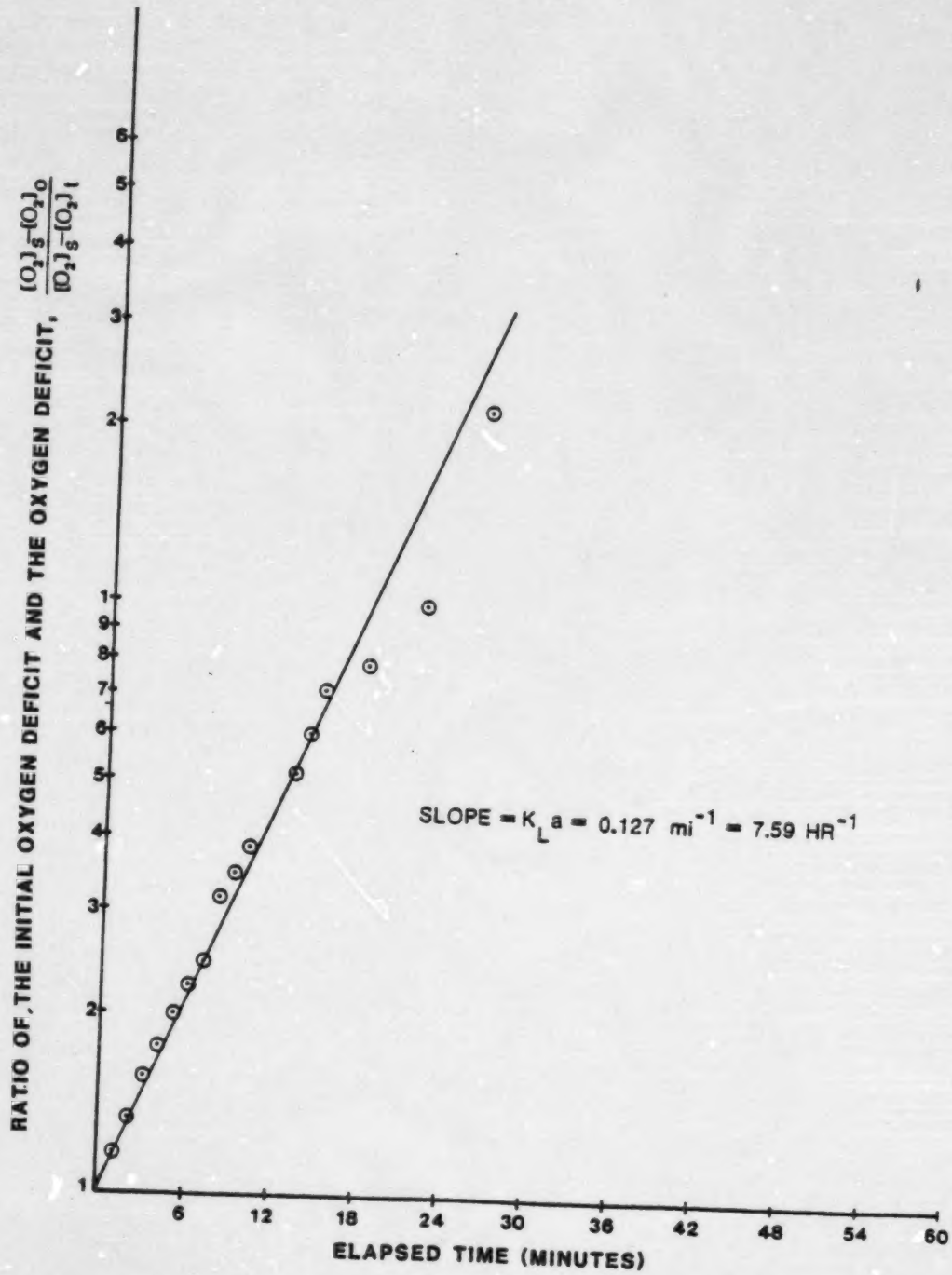

FIG. 4. DETERMINATION OF THE REAERATION RATE CONSTANT, $K_L a$, IN EXPERIMENT ST-3

TABLE 2. EXPERIMENTAL DATA OBTAINED DURING STRIPPING RATE MEASUREMENTS FOR TOLUENE

Matrix tested	Experiment No.	Air flow rate (L/min)	Material balance (%)	Stripping rate constant ($K_a sta[hr^{-1}]$)	Reaeration rate constant ($K_L a[hr^{-1}]$)	$\frac{K_a st_a}{K_L a}$	Surface tension (dynes/cm)
Toluene in water	ST-1	2	104.2	1.13	2.76		68.61
	ST-2	2	99.8	1.16	7.65	0.151	67.36
	ST-3	2	120.0	0.97	7.13	0.136	63.96
	ST-4	4	105.0	1.84	14.00	0.132	57.95
	ST-5	8	82.3	3.98	31.50	0.126	61.30
Toluene + Triton DF-12 (0.01%)	ST-6	2	76.3	0.72	1.81	0.397	34.88
	ST-13	2	123.0	0.58	1.69	0.344	35.80
	ST-7	4	62.8	1.53	4.58	0.335	35.12
	ST-12	4	102.0	1.46	4.61	0.318	36.17
	ST-18	5	90.7	1.99	6.59	0.302	37.00
	ST-17	6	100.5	2.22	8.01	0.277	35.82
	ST-8	8	93.4	2.67	12.86	0.208	31.7
Toluene + Marasperse (1%)	ST-9	2	99.5	0.58	0.91	0.641	51.70
	ST-10	4	80.9	1.67	4.29	0.389	59.30
	ST-11	8	102.0	3.31	9.30	0.356	56.93
(Mar.[a] (0.5%)	ST-19	2	110.6	0.63	1.53	0.412	61.57
Toluene + 1-octanol (1000 mg/L)	ST-14	2	(268) ?	0.61	2.32	0.263	32.73
	ST-15	8	106	2.48	17.28	0.144	32.10
Toluene + salt NaCl (5000 mg/L)	ST-16	2	154	0.87	4.54	0.191	66.76
Toluene + FC[b] + D-foam (602 mg/L)	ST-43	2	c	0.71	2.12	0.335	67.33
Toluene + non-viable biomass (1500 mg/L)	ST-44	2	c	0.59	2.12	0.278	60.5
Toluene + FC[b] + D-foam (602 mg/L) + Triton DF-12 (0.01%) + non-viable biomass	ST-45	2	118	0.58	1.19	0.488	43.1
Toluene + 1,4-dichloro-benzene	ST-46	2	83	0.89	5.10	0.175	70.33

[a]Marasperse.

[b]Foul condensate.

[c]Off-gas analysis was not performed, therefore no material balance was obtained.

showed little difference. For convenience, tap water was used for all stripping experiments, and referred to as pure water.

Periodic gas samples analyzed for toluene were integrated over the runs and compared with initial and end values of toluene in the liquid phase to determine the material balance. The material balances in the toluene runs were acceptable with the exception of the 1-octanol experiment, ST-14. That high value may be related to the extraction of toluene by octanol from the liquid phase which leads to low aqueous phase measurements.

The material balance was acceptable in all dichlorobenzene experiments (Table 3) except experiment ST-30 with dichlorobenzene in Tamol at an air flow rate of 8 L/min and in experiment ST-31 with dichlorobenzene in foul condensate. In these two experiments, Tamol and foul condensate caused excessive foaming problems in the reactor. Therefore, a 2-gal polyethylene foam trap was added at the outlet air line before the condenser to reduce the possibility of contaminating the off-gas samples in the bubblers. In experiment ST-30, foaming with high air flow rate 8 L/min probably carried 1,4-dichlorobenzene into the bubblers by foam fractionation. In experiment ST-31, leaking in the foam trap probably was the result of the low value in the material balance.

The stripping rate constant of methyl ethyl ketone seemed to be affected very little by the addition of other substances to water. Triton DF-12 at 0.01% and 0.001%, D-Foam ST. in foul condensate, and nonviable biomass are examples of this. This effect appeared small when compared with the effect of air flow-to-liquid volume of the solution and again, $K_a{}^{st}a$ seemed to vary linearly with it. Values of the stripping rate constant, $K_a{}^{st}a$, and oxygen reaeration rate constant K_La of all methyl ethyl ketone experiments are listed in Table 4.

Phenol stripping rates (Table 5) were determined by gas analysis, since water evaporation makes liquid phase analysis unreliable. The material balance for phenol experiments was very low, probably because phenol strips more rapidly than the water evaporation rate.

All stripping experiments were conducted at temperatures between 17.0°C to 23.6°C. Gaudy[9] stated that the stripping rate constant values remain essentially constant for a relative increase in temperature interval of 5 to 10°C;

TABLE 3. EXPERIMENTAL DATA OBTAINED DURING STRIPPING RATE MEASUREMENTS FOR 1,4-DICHLOROBENZENE

Matrix tested	Experiment No.	Air flow rate (L/min)	Material balance (%)	Stripping rate constant ($K_a st_a[hr^{-1}]$)	Reaeration rate constant ($K_L a[hr^{-1}]$)	Surface tension (dynes/cm)
DCB in water	ST-20	2	100	0.32	4.83	60.54
	ST-21	4	129	0.91	16.84	65.63
	ST-25	8	110	1.94	33.91	57.70
DCB + Triton DF-12(0.01%)	ST-24	2	108	0.33	2.03	36.98
	ST-27	4	100	0.77	5.20	36.40
	ST-26	8	108	1.44	15.75	37.45
DCB + Tamol 731 (0.01%)	ST-28	2	83	0.41	2.42	58.12
	ST-29	4	108	1.17	9.39	58.70
	ST-30	8	129	2.03	17.75	59.74
DCB + salt NaCl (5000 mg/L)	ST-32	2	101	0.53	5.46	53.0
DCB + foul condensate	ST-31	2	~~45.7~~ 46	0.31	2.90	57.70
DCB + Toluene	ST-46	2	83.0	0.33	5.10	70.33
DCB + nonviable biomass (1500 mg/L)	ST-47	2	~~99.6~~ 100	0.32	2.22	57.07

TABLE 4. EXPERIMENTAL DATA OBTAINED DURING STRIPPING RATE MEASUREMENTS FOR METHYL ETHYL KETONE

Matrix tested	Experiment No.	Air flow rate (L/min)	Material balance (%)	Stripping rate constant ($K_a^{st}a[hr^{-1}]$)	Reaeration rate constant ($K_La[hr^{-1}]$)	Surface tension (dynes/cm)
MEK in water	ST-33	8	89	0.038	30.24	57.46
	ST-34	4	93	0.019	12.80	59.48
	ST-35	2	104	0.009	5.26	60.56
MEK + Triton DF-12 (0.01%)	ST-36	4	89	0.018	4.74	36.10
	ST-37	2	101	0.008	1.69	36.42
	ST-38	8	102	0.035	13.12	36.20
MEK + Triton DF-12 (0.001%)	ST-39	2	90	0.011	1.78	42.93
	ST-40	4	90	0.019	4.96	45.53
MEK + FC[a] + D-foam (602 mg/L)	ST-41	2	97	0.009	0.81	63.30
MEK + nonviable mass (1500 mg/L)	ST-42	2	90	0.013	2.40	63.5

[a] Foul condensate.

TABLE 5. EXPERIMENTAL DATA OBTAINED DURING STRIPPING RATE MEASUREMENTS FOR PHENOL

Matrix tested	Experiment No.	Air Flow rate (L/min)	Material balance (%)	Stripping rate constant ($K_a st_a$ [hr^{-1}])	Reaeration rate constant ($K_L a$ [hr^{-1}])	Surface tension (dynes/cm)
Phenol in water	ST-22	4.0	16.8	8.096×10^{-5}	13.67	53.63
	ST-23	2.0	7.0	5.115×10^{-5}	7.08	64.02

therefore, it can be assumed that temperature had little effect on these experimental stripping rate constant values.

Stripping Predictive Method

The ratio of the stripping rate constant over the oxygen reaeration rate constant, $K_a{}^{st}a/K_La$, seemed constant within the toluene experiment in water, as predicted by Smith et.al.[4,5] for high volatility compounds in natural waters. But this constant value varied greatly with the addition of various chemicals. The ratio, $K_a{}^{st}a/K_La$ = constant, does not appear to be a reliable predictor for stripping rates in actual wastewater.

The results from Tables 2, 3, 4, and 5 for toluene, 1,4-dichlorobenzene, and methyl ethyl ketone, each at 3 levels of air flow rates of 2, 4, and 8 L/min and also for phenol in pure water at air flow rates of 2 L/min and 4 L/min may be correlated to produce a simple power relationship. This relationship incorporates the Henry's law constant and the air flow-to-liquid volume ratio to directly yield the stripping rate constant for pure water systems.

$$K_a{}^{st}a \cdot \frac{V}{Q} = b(H_c)^m \qquad (8)$$

Where:

$K_a{}^{st}a$ = stripping rate constant (hr^{-1}),

H_c = Henry's law constant $\left(\frac{\text{torr L}}{\text{g-mole}}\right)$,

V = volume of the liquid in the reactor (L),

Q = air flow rate (L/min),

b and m = power function constants, and

$K_a{}^{st}a \cdot \frac{V}{Q}$ = stripping rate parameter.

Table 6 presents the findings for these equations by fitting power equations of the form, $y = bx^m$. For pure water systems, $b = 3.71 \times 10^{-3}$ and $m = 1.045$ with 11 data points yielding a correlation coefficient, r^2, of 0.991.

TABLE 6. EMPIRICAL RELATIONSHIP BETWEEN STRIPPING KINETIC RATE CONSTANT AND HENRY'S LAW CONSTANT FOR DIFFUSED AERATION SYSTEM

$$K_a{}^{st}{}_a \cdot \frac{V}{Q} = (H_c)^m$$

Data included	Power equation constants b	m	Number of data points	Regression coefficient r^2
Toluene, 1,4-dichlorobenzene, and MEK in pure water at air flow rate 2,4,8 L/min and phenol in pure water at air flow rate 2,4 L/min	3.71×10^{-3}	1.045	11	0.991
Toluene, DCB, and MEK in Triton DF-12 (0.01%) at air flow rate 2,4,5,6, and 8 L/min	9.30×10^{-3}	0.872	11	0.997

Use of the dimensionless Henry's law constant yields the simple dimensionless relationship:

$$K_a{}^{st}a \ \frac{V}{Q} = H_i \qquad (9)$$

Reconciliation of this equation with two-film theory suggests that mass transfer in the system is very rapid, reaching equilibrium quickly. This result is related to the turbulence in an "engineered" system and leads to the conclusion that stripping in the dispersed phase system (gas or liquid) may be fundamentally different from volatilization, where mass transfer processes are limiting.

Table 6 also presents the power function constants for three compounds in surfactant Triton DF-12 solution with 11 data points and a high regression coefficient value.

This model for our stripping PFMs was tested in the lab-scale activated sludge study using toluene in a continuous system with a liquid volume of 11 L and a mean air flow rate of 2 L/min in a similar bubble size distribution. The predictor developed in this study for pure water, $K_a{}^{st}a \cdot V/Q = 3.71 \times 10^{-3}(H_c)^{1.045}$, gave the stripping rate constant predicted for toluene in the lab-scale activated sludge system of 2.7 hr^{-1}. This predicted value as compared to an experimental mean of 2.4 hr^{-1} for both biological and nonbiological systems provides good agreement. The lab scale systems operated during several upset conditions, but the stripping rate constant remained relatively constant.

From the model of this study, $K_a{}^{st}a \cdot V/Q = 3.71 \times 10^{-3} (H_c)^{1.045}$, the predicted values of $K_a{}^{st}a$ for different compounds were calculated and compared with the values of the stripping rate constant $K_a{}^{st}a$ calculated from Kincannon,[10] Roberts,[11] and Weber[12] for different chemicals in nonbiological systems. These values are presented in Table 7 and they are in agreement with the predictor.

Petrasek[13] performed a pilot-plant study to evaluate the removal and partitioning of volatile organic priority pollutants in publicly owned treatment works (POTWs). The pilot plant consisted of a primary clarifier, a 58.32 m^3

TABLE 7. COMPARISON OF REPORTED VALUES OF THE STRIPPING RATE CONSTANT, $K_a{}^{st}{}_a$

Compound	Henry's law constant $\frac{torr\ L}{g\text{-}mole}$	Values of $K_a{}^{st}{}_a(hr^{-1})$ calculated from reported data			$K_a{}^{st}{}_a(hr^{-1})$ predicted from this study
		Kincannon[10]	Roberts[11]	Weber[12]	
Methylene chloride	2424[a]	9.73			6.14
Chloroform	2388[b]		2.92		1.95
1,2-Dichloropropane	2143[a]	4			4.50
Trichloroethylene	7174[b]		3.32		6.16
Benzene	4218[a]			5.46	9.11
Benzene	4218[a]	8.58			10.00
1,1,1-Trichloroethane	3033[b]		3.27		2.51
Chlorobenzene	2359[c]			3.72	4.97
Tetrachloroethylene	15480[b]		3.27		13.80
o-Xylene	3034[b]			4.38	6.46
Toluene	2769[c]			5.58	5.87
Ethylbenzene	4890[b]			6.18	10.60
Phenol	0.25[c]	0.0011			0.0003
1,2-Dichlorobenzene	1149[c]			2.46	2.34

[a]From ref. 13.

[b]Calculated by using Dilling's equation[7] with solubility and vapor pressure values from ref. 14.

[c]Calculated by using Dilling's equation[7] with solubility and vapor pressure values from ISHOW data base.[8]

plug flow aeration basin, followed by a secondary clarifier. Conventional coarse bubble diffusers were used with a nominal air flow of 57 L/sec. Table 8 lists the values of the stripping rate constant $K_a st_a$ calculated from Petrasek's reported data. These calculated values are lower and range from 0.6% for tetrachloroethylene to 94% for dibromochloromethane, as shown in Table 8 for comparison with the predicted values from this study.

These differences are not surprising. Aqueous phase data were measured only at the aeration basin influent and effluent, even though the plant was a plug flow design. An average of influent and effluent was used in our calculations and was probably much higher than the true mean C_a for the plant. For application of this predictor to plug flows or batch processes, a true mean liquid concentration would have to be determined by sampling the liquid phase at various points within the process, or in the case of batch design, sampling of the liquid over the batch interval. Influent and effluent data are inadequate for prediction of stripping in batch and plug flow reactors. Further discussion of this issue may be found in the project report.[1]

Effect of Contaminants

To illustrate the relative effects of varous contaminants on the stripping rate, the mean values of the stripping rate parameter, $K_a st_a \cdot V/Q$, for all experiments were calculated. In Fig. 5 through 8, the percentages of the mean of $K_a st_a \cdot V/Q$ of toluene, 1,4-dichlorobenzene and methyl ethyl ketone in various test contaminant systems to pure water are plotted against the mean surface tensions of the related solutions. Standard deviations as a measure of error are also shown.

Figure 5 shows the effects of salts and oils, Fig. 6 shows the effect of surfactants, Fig. 7 shows the effect of biomass, and Fig. 8 shows the effect of a waste stream such as foul condensate on the pure water stripping rate.

Most contaminants caused a reduction in the stripping rate. Systems showing increases are 1,4-dichlorobenzene (DCB) + salt and methyl ethyl ketone (MEK) with Triton DF-12 and with biomass. The high value in the DCB + salt experiment may be caused by a decrease in water solubility related to the "salting out" effect. A lower solubility would tend to increase the Henry's law constant and

TABLE 8. COMPARISON OF REPORTED VALUES OF THE STRIPPING RATE CONSTANT, $K_a{}^{st}{}_a$

Compound	Henry's law constant $\frac{\text{torr L}}{\text{g-mole}}$	Values of $K_a{}^{st}{}_a(hr^{-1})$ calculated from Petrasek's reported data	Values of $K_a{}^{st}{}_a(hr^{-1})$ predicted from this study	Percent Agreement $\frac{K_a{}^{st}{}_a \text{ calc.}}{K_a{}^{st}{}_a \text{ pred.}}$
1,1-Dichloroethene	11400[a]	0.088	3.766	2.3
Chloroform	2388[b]	0.040	0.736	5.4
Carbon tetrachloride	22952[a]	0.071	7.822	0.9
1,2-Dichloropropane	2143[a]	0.038	0.657	5.8
Trichloroethylene	7174[b]	0.062	2.321	2.7
1,1,2-Trichloroethane	562[a]	0.026	0.162	16.1
Dibromochloromethane	593[a]	0.162	0.172	94.2
Benzene	4218[a]	0.026	1.333	2.0
1,1,1-Trichloroethane	3033[b]	0.075	0.944	7.9
Bromodichloromethane	1611[a]	0.127	0.488	26.0
Chlorobenzene	2359[c]	0.006	0.726	0.8
Tetrachloroethylene	15480[b]	0.031	5.184	0.6
1,1,2,2-Tetrachloroethane	289[a]	0.031	0.081	38.3
Toluene	2769[c]	0.024	0.859	2.8
Ethylbenzene	4890[b]	0.025	1.555	1.6

[a] From ref. 13.

[b] Calculated by using Dilling's equation[7] with solubility and vapor pressure values from ref. 14.

[c] Calculated by using Dilling's equation[7] with solubility and vapor pressure values from ISHOW data base.[8]

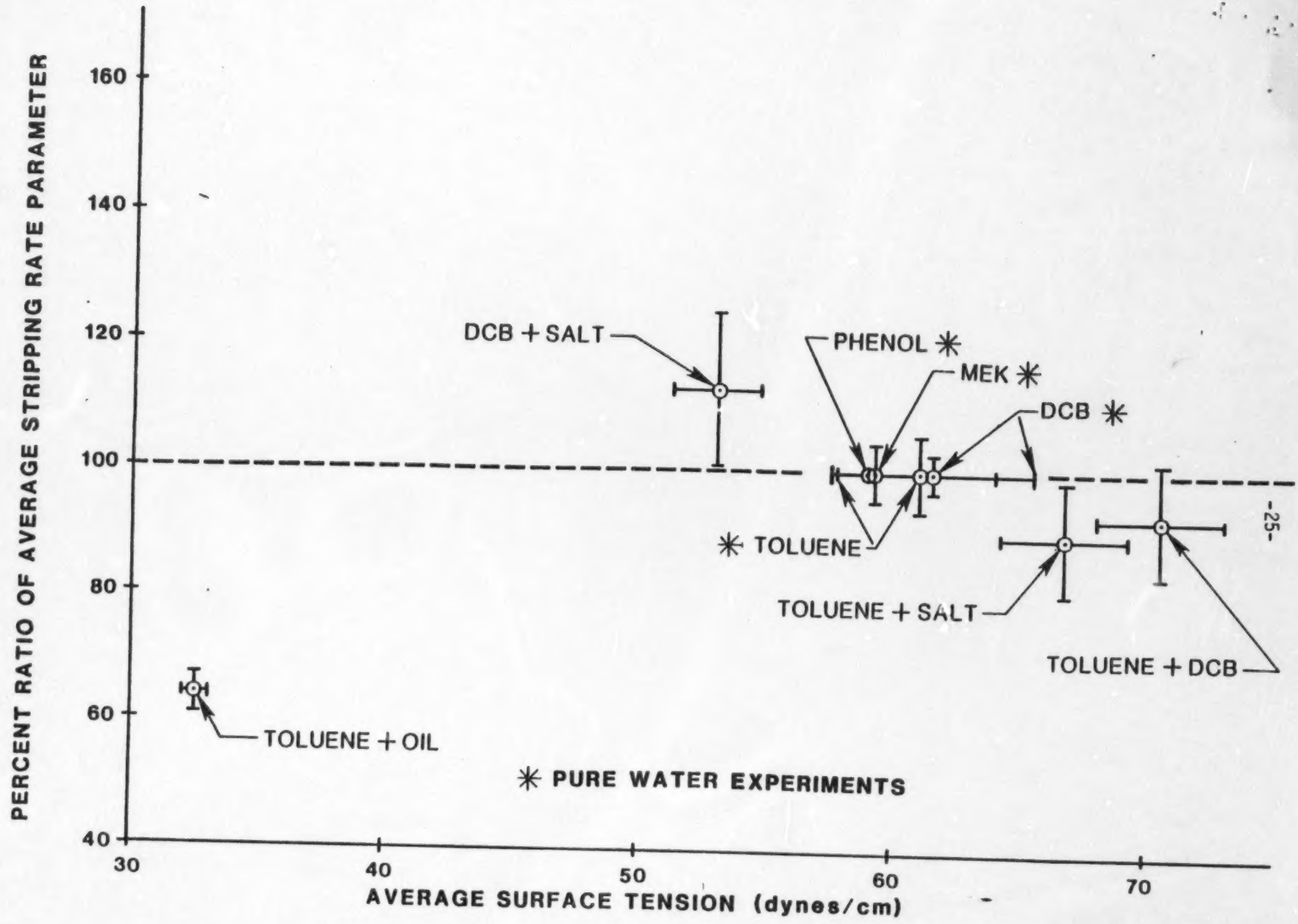

FIG. 5. THE EFFECT OF CONTAMINANTS ON THE SUBSTRATE STRIPPING RATE (PURE WATER, OIL, AND SALT EXPERIMENTS)

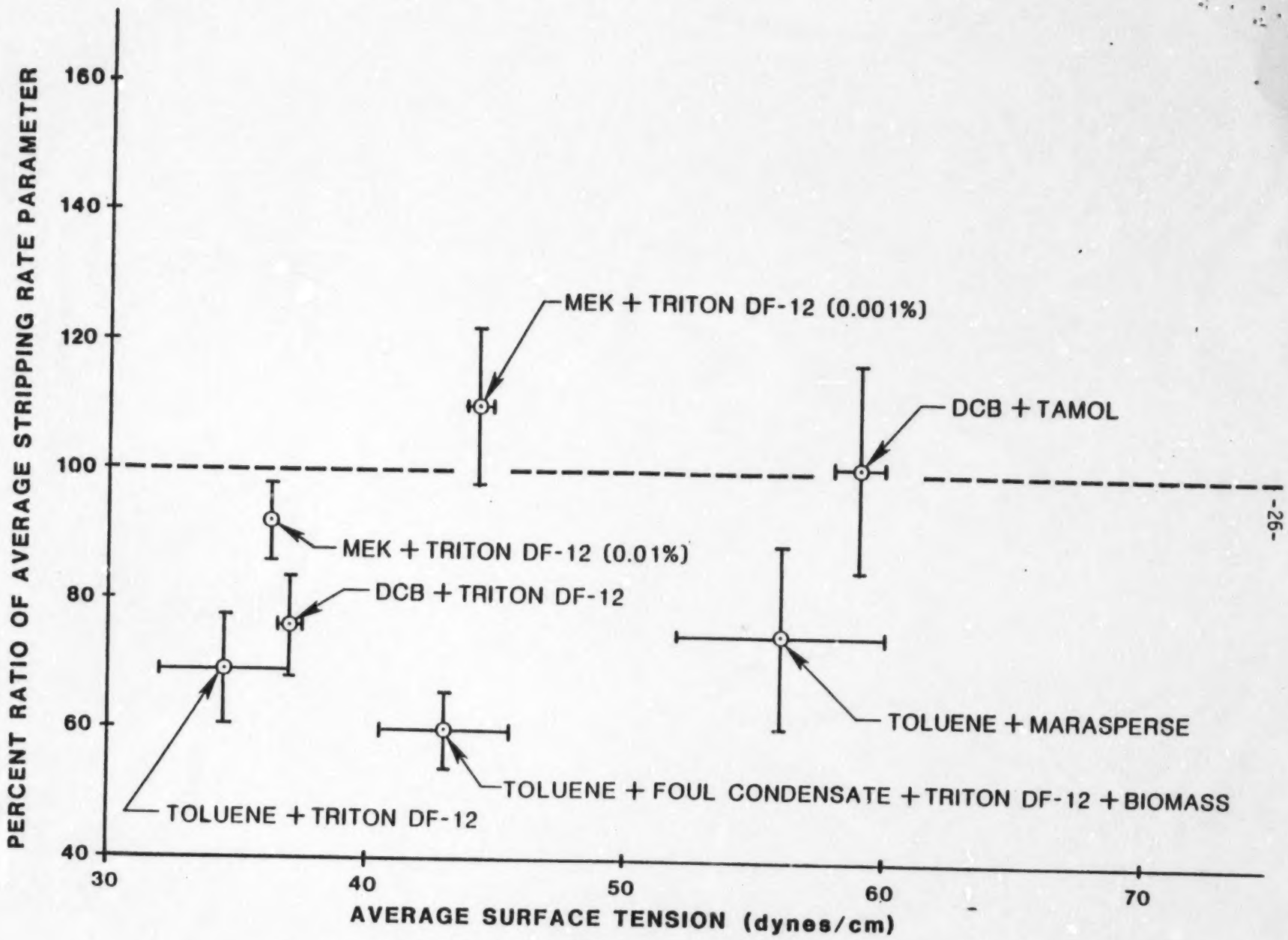

FIG. 6. THE EFFECT OF CONTAMINANTS ON THE SUBSTRATE STRIPPING RATE (TRITON DF-12, MARASPERSE, AND TAMOL SURFACTANT EXPERIMENTS)

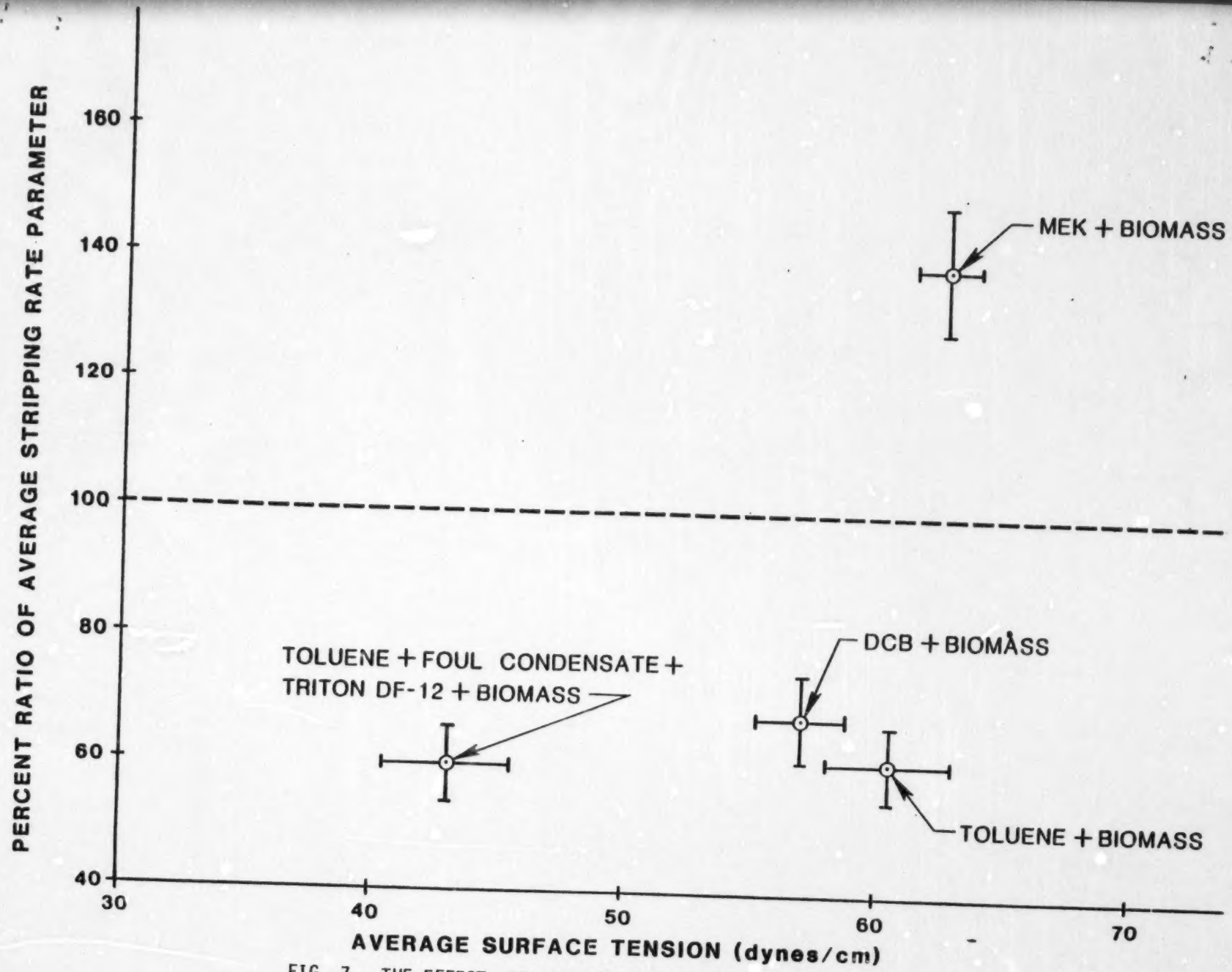

FIG. 7. THE EFFECT OF CONTAMINANTS ON THE SUBSTRATE STRIPPING RATE (BIOMASS EXPERIMENTS)

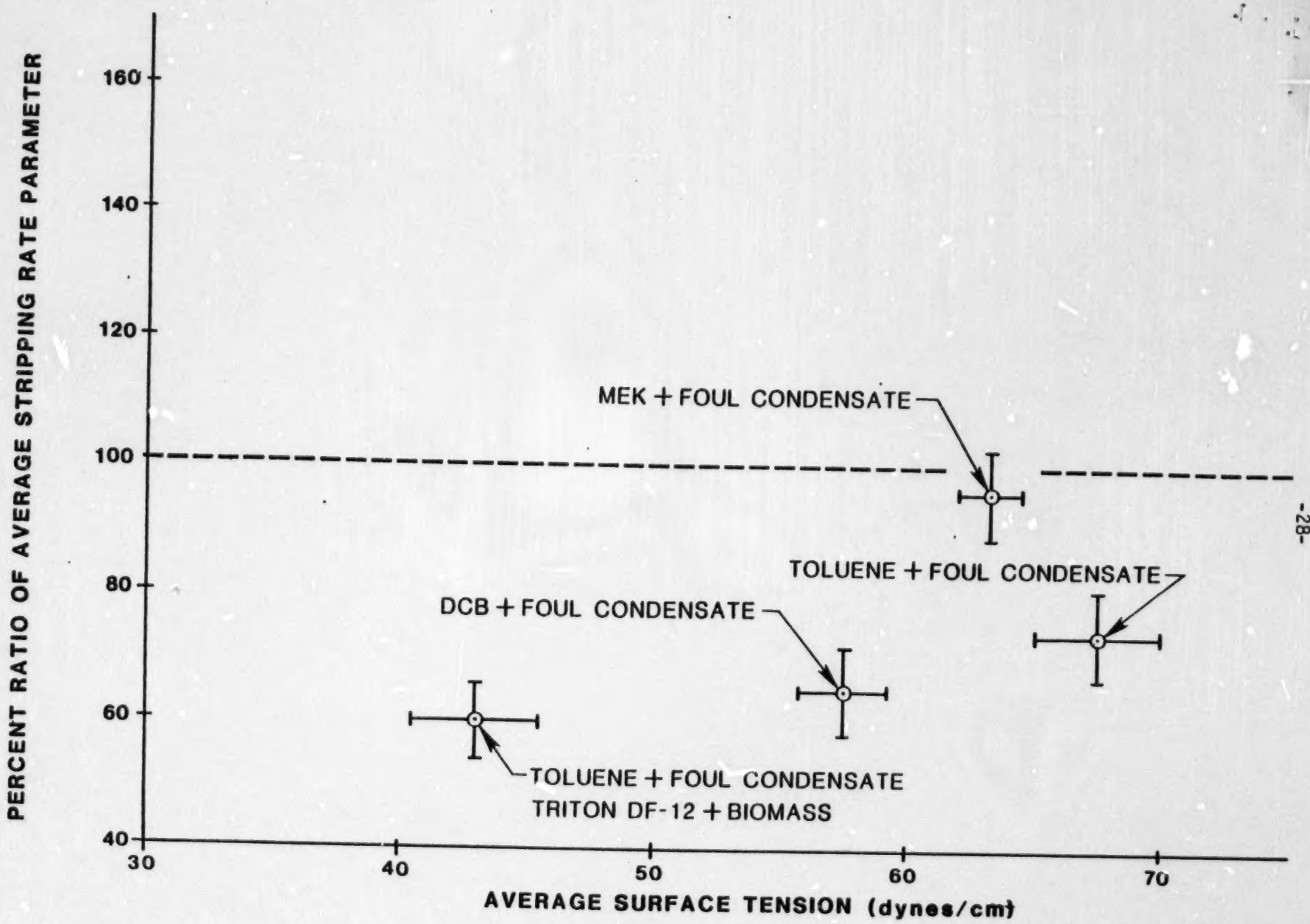

FIG. 8. THE EFFECT OF CONTAMINANTS ON THE SUBSTRATE STRIPPING RATE (FOUL CONDENSATE EXPERIMENTS)

the stripping rate. The high MEK + Triton DF-12 data may be artificial. The error bands for the stripping rate parameter ratio overlap those of pure water MEK experiments.

No explanation is given for the high MEK + biomass data. The biomass was tested and verified as nonviable using a respirometric technique. Therefore, no bio-oxidation interference is suspected.

In any case, the stripping rate related to other contaminants in the wastewater may vary ±50% when compared with the pure water. The effects also seem to be stronger for the higher volatility compounds.

CONCLUSIONS

An approach for stripping fate predictions of organic chemicals in biological processes has been developed. Conclusions that may be drawn from this project follow:

1. The method developed in this work offers a simpler approach for estimating stripping rates in pure water and wastewater than other approaches based on the two-film theory of mass transfer. This method incorporates the Henry's law constant and the air flow-to-liquid volume ratio to directly yield the stripping rate constant for pure water systems. Equations predicting the stripping rate constant from the compound Henry's law constant follow the form of $K_a st_a \cdot V/Q = 3.71 \times 10^{-3} (H_c)^{1.045}$ for a pure water system.

2. The presence of surfactants, salts, oils, and nonviable biomass was found to vary the stripping rate, but in no case was the effect more than ±50% when compared with pure water. The effect seemed to be the strongest for the higher volatility compounds.

3. The values of the stripping rate constant, $K_a st_a$, predicted from the model in this study seem to agree reasonably well with previously reported values. This suggests the possibility of application beyond the compounds studied herein.

4. The stripping predictive fate method was tested in continuous lab-scale activated sludge units. The measured toluene stripping rate was found to be consistent with the predicted toluene stripping rate constant. This further substantiates that the stripping predictive fate method may be useful for prediction of compound stripping in continuous "real world" systems.

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